

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
22 February 2001 (22.02.2001)

PCT

(10) International Publication Number  
**WO 01/12149 A1**

(51) International Patent Classification<sup>7</sup>: **A61K 7/48**

(21) International Application Number: **PCT/EP00/06799**

(22) International Filing Date: **14 July 2000 (14.07.2000)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
**60/148,775 13 August 1999 (13.08.1999) US**

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **COSMETIC STRIPS WITH TEMPERATURE DEPENDENT COLOUR CHANGE**

(57) Abstract: An adhesive cosmetic strip is provided which includes a flexible water-insoluble substrate, an adhesive composition deposited onto the substrate, and a non-liquid crystal thermochromic substance. The thermochromic substance may be impregnated into the substrate or dispersed within the adhesive composition. When applied to the skin, the strip is warmed from body heat or may undergo a reaction between water and an exothermic or endothermic agent held within the strip.

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COSMETIC STRIPS WITH  
TEMPERATURE DEPENDENT COLOUR CHANGE

5                                    **BACKGROUND OF THE INVENTION**

Field of the Invention

The present invention relates to cosmetic dermal strips or  
10 patches which provide consumers with a colour change  
indicator as a sensorial signal.

The Related Art

15    Cosmetics are often provided with consumer perceivable  
sensorial signals. Most common of these signals are  
fragrances. Pleasing odor is often the single most  
important attribute inducing re-purchase by a consumer.  
Other sensorial attributes are also significant in cosmetic  
20 chemistry. The skin-feel of a product is highly important.  
Creams, lotions, gels and pastes often are judged for their  
efficacy by the tactility of their feel. Silky, non-residue  
leaving cosmetics are much preferred over tacky ones, and  
the consumer may relate those aesthetics to actual  
25 pharmacological performance.

Sometimes the sensorial attribute is that of temperature.  
Coolness is imparted to toothpastes and aftershave lotions  
through the presence of camphor, menthol or menthol  
30 derivatives such as menthol lactate. Some formulations  
signal efficacy through a temperature increase. Inclusion

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of capsaicin, an alkaloid extracted from capsicum, gives a brief temperature rise sensation to the human neural system.

Dermal patches or strips have recently become popular as  
5 delivery vehicle systems for cosmetic compositions. For instance, WO 98/42303 (Crotty et al.) describes a dry-to-the-touch keratotic plug remover strip. Upon wetting, the strip turns tacky and mobile. This product is placed on the bridge of the nose or other areas of the face requiring  
10 keratotic plug removal. Within a short time period, water evaporates from the wetted adhesive forming a dry film. The consumer then peels the film from the face along with unwanted plugs bonded thereto. The amounts of water applied by consumers may vary. Drying times are therefore also  
15 variable. A sensorial signal would be helpful for the consumer to know when to begin removal of the film.

Exothermic and endothermic reactions are other sources of temperature signaling. U.S. Patent 5,861,440 (Gohla et al.)  
20 reports use of sugars, especially xylitol, for inducing a cooling sensation when contacted with water. Generation of exothermic heat is reported in U.S. Patent 4,379,143 (Sherry et al.), U.S. Patent 4,626,550 (Hertzenberg), U.S. Patent 4,362,715 (Strianse et al.) and U.S. Patent 3,250,680  
25 (Menkart et al.). Each of these documents describes use of an aluminosilicate interacting with water to release momentary heat.

Other types of sensorial signals have been sought for  
30 incorporation into cosmetics. The signals should either

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provide an independently new effect or complement those that have traditionally been employed.

Accordingly, it is an advantage of the present invention to  
5 be able to provide cosmetic products, especially dermal strips or patches with a new sensorial signal.

Another advantage of the present invention is to be able to provide a cosmetic product, especially dermal strips or  
10 patches with a sensorial signal, which may augment other sensory or emotive aesthetics of such products.

Another advantage of the present invention is to be able to provide a cosmetic product, especially dermal strips or  
15 patches uniquely suited for incorporation with flexible substrates and which provide a timing mechanism for application, rub-in or removal of the product from a consumer's skin.

20 These and other advantages of the present invention will become more readily apparent from consideration of the following summary and detailed discussion.

#### **SUMMARY OF THE INVENTION**

25

The present invention provides an adhesive cosmetic strip, which comprises:

- (i) a flexible water-insoluble substrate;
- (ii) an adhesive composition deposited onto the  
30 substrate; and

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- (iii) a non-liquid crystal type thermochromic substance incorporated into at least one of the substrate or the adhesive composition, the thermochromic substance changing colour in response to a change of temperature after the strip has contacted a user's skin.

#### DETAILED DESCRIPTION OF THE INVENTION

A visual sensorial signal suitable for use with dermal strips or patches has been found. The present invention relates to the use of non-liquid crystal type thermochromic substances whose colour changes in response to a change in temperature. The substances may either be incorporated into the flexible substrate structurally supporting the strip or patch or may be formulated with the adhesive.

Thermochromic substances of the present invention have one colour at room temperature but undergo a colour change at either higher or lower temperatures. Illustrative of such substances are double salts comprising a transition metal such as cobalt, nickel or manganese in combination with an aminic amide such as hexamethylenetetramine. These double salts discolour on releasing water when heated and resume the original colour on absorption of moisture when cooled. Other examples include mercury iodide, double complex salts of mercury iodide with other metallic iodides, heavy metal compounds such as lead chromate and ammonium metavanadate, dixanthylene and bianthrone. All of these types of materials are useful in the present invention but are not the most preferred.

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Liquid crystals including cholesteric and nematic liquid crystals are not particularly suitable for use in the present invention. The term "thermochromic substances" as  
5 used herein is not, therefore intended to encompass such liquid crystals. These crystals have low colour density, poor colour selectivity and are quite expensive.

The thermochromic substances which are most preferred for  
10 use in the present invention are based on compositions comprising: (1) an acid-responsive chromogenic material; and (2) an acidic material; optionally combined with (3) a solvent for dilution of the other materials.

15 Suitable acid-responsive chromogenic materials include triphenylmethanephthalide compounds, phthalide compounds, phthalan compounds, acyl-leucomethylene blue compounds, fluoran compounds, triphenylmethane compounds, diphenylmethane compounds and spiropyran compounds.

20 Examples of suitable acid-responsive chromogenic materials include the following:

3,6-dimethoxyfluoran (yellow), 3,6-dibutoxyfluoran, 3-diethylamino-6,8-dimethylfluoran, 3-chloro-6-  
25 phenylaminofluoran (orange), 3-diethylamino-6-methyl-7-chlorofluoran (vermilion), 3-diethylamino-7,8-benzofluoran (pink), 2-anilino-3-methyl-6-diethylamino-fluoran (blue), 3,3',3''-tris(p-dimethylaminophenyl)phthalide (purplish blue), 3,3'-bis(p-dimethylaminophenyl)phthalide (green), 3-  
30 diethylamino-7-phenylaminofluoran (black), 3,3-bis(p-diethylaminophenyl)-6-dimethylaminophthalide, 3-(4-

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diethylaminophenyl)-3-(1-ethyl-2-methylindol-3-yl)phthalide, 3-(4-diethylamino-2-methyl)phenyl-3-(1,2-dimethylindol-3-yl)phthalide, 2'-(2-chloroanilino)-6'-dibutylaminospiro-[phthalido-3,9'-xanthene] and mixtures thereof.

5

The acid-responsive chromogenic material is used in an amount of from about 0.1 to about 50% by weight of the thermochromic substance.

- 10 The acidic material mentioned may include 1,2,3-benzotriazole compounds, phenol compounds, thiourea compounds, oxo-aromatic carboxylic acids and mixtures thereof. Specific examples include: 1,2,3-benzotriazole, 1,2,3-triazole ethyl 4-methyl-5-carboxylate, 4(5)-hydroxy-  
15 1,2,3-triazole, 5(6)-methyl-1,2,3-benzotriazole, 5(6)-chloro-1,2,3-benzotriazole, 5(6)-methoxy-1,2,3-benzotriazole, 4(7)-nitro-1,2,3-benzotriazole, 5(6)-carboethoxy-1,2,3-benzotriazole, 5-methoxy-7-nitro-1,2,3-benzotriazole, 4-amino-1,2,3-benzotriazole, 4-benzoylamino-  
20 1,2,3-benzotriazole, 4,5,6,7-tetrachloro-1,2,3-benzotriazole, 4-hydroxy-1,2,3-benzotriazole, naphtho-1,2,3-benzotriazole, 5,5'-bis-1,2,3-benzotriazole, 4(7)-sulfoanilino-1,2,3-benzotriazole, 1,2,3-triazole diethyl dicarboxylate, phenol, nonylphenol, bisphenol A, bisphenol  
25 F, 2,2'-biphenol, beta-naphthol, 1,5-dihydroxynaphthalene, alkyl p-hydroxybenzoates, phenol resin oligomer and mixtures thereof.

- The acidic material is used in an amount of from about 0.1  
30 to about 50% by weight of the thermochromic substance.

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The thermochromic substances, each containing an acid-responsive chromogenic material and an acidic material, are preferably diluted with a solvent before use. The use of a solvent renders the substance responsive to changes in temperature with greater sensitivity and definition. The solvents which can be used for the thermochromic substance includes, among others, C<sub>8</sub>-C<sub>40</sub> alcohols, alcohol-acrylonitrile adducts, azomethine compounds, esters and mixtures of these. Among specific examples of the solvent are decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, lauryl alcohol-acrylonitrile adduct, myristyl alcohol-acrylonitrile adduct, stearyl alcohol-acrylonitrile adduct, benzylidene-p-toluidine, benzylidene-butylamine, octyl caprate, decyl caprate, myristyl caprylate, decyl laurate, lauryl laurate, myristyl laurate, decyl myristate, lauryl myristate, cetyl myristate, lauryl palmitate, cetyl palmitate, stearyl palmitate, cetyl myristate, lauryl palmitate, cetyl palmitate, stearyl palmitate, cetyl p-t-butylbenzoate, stearyl 4-methoxybenzoate, dilauryl thiodipropionate, dimyristyl thiodipropionate, stearyl benzoate, benzyl stearate, dibenzyl thiodipropionate, distearyl thiodipropionate, benzyl benzoate, glycerol trilaurate and mixtures thereof.

25

The amount of the solvent may range from 0 to about 90%, preferably from about 0.1 to 50% by weight of the thermochromic substance.

30

Reversibly variable colour thermochromic substances optionally can be microencapsulated before incorporation



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into the adhesive cosmetic strip. Microencapsulation can be accomplished in any conventional manner. For example, using the reversibly variable colour material, a shell-forming polymer and, where necessary, a surfactant, protective colloid, pH control agent, electrolyte, etc., the desired microcapsules can be prepared in water by any of interfacial polymerization, in situ polymerization, coacervation, air suspension, interfacial precipitation and other techniques. By such processes, microcapsules including the reversibly variable color material and measuring from about 1 to 50  $\mu\text{m}$  in diameter can be obtained. It is also possible to provide double- or multiple-walled microcapsules by using one, two or more of the microencapsulation techniques mentioned above. The preferred shell-forming material includes a polyamine and a carbonyl compound for forming a polyurea shell, a polybasic acid chloride and a polyamine for forming a polyamide shell, a polyisocyanate and a polyhydroxy compound for forming a polyurethane shell, a polybasic acid chloride and a polyhydroxy compound for forming a polyester shell, an epoxy compound and a polyamine for forming an epoxy resin shell, a melamine-formaldehyde prepolymer for forming a melamine resin shell and a urea-formaldehyde prepolymer for forming a urea resin shell, as well as ethylcellulose, polystyrene, polyvinyl acetate and so on.

Microcapsule delivery systems can be formulated into the adhesive composition or into the flexible substrate. Incorporation into a fibre-structured fabric is accomplished by co-compounding the microcapsules with the fibre resin in a molten form (common vat or extruder). Incorporation into non-fibrous sheets can be accomplished by hot melt casting

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of the thermochromic encapsulates with plastic resin forming films. In all these instances, the shell of the microcapsules is preferably made of a thermosetting material that has superior heat resistance.

5

The above information with respect to the preferred thermochromic substances may be found in U.S. Patent 4,717,710, U.S. Patent 4,851,282 and U.S. Patent 5,431,697, all herein incorporated by reference. Substances described therein or at least similar are available from the assignee, Matsui International Company, Inc., Gardena, California. A commercially available substance from Matsui International suitable for the present invention is Chromicolor AQ Ink, especially Type 27, which is available in twelve colours.

15

Type 27 has a colour that appears below 24°C and changes above 33°C. Thus, a blue variant of Type 27 will hold colour until a dermal strip is moisturized. As temperature rises, the blue will fade to a colourless mode and return eventually to blue when the system has cooled. Other useful Chromicolor AQ Inks are Type 35 where color is maintained below 27°C and disappears above 36°C. Type 25 has colour appearing below 22°C but disappearing above 31°C. Endothermic reactions may usefully employ Type 07 where the system is colourless above 5°C but colour appears below minus 4°C.

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Flexible water-insoluble substrates are another essential element of the present invention. By "water insoluble" is meant that the substrate does not dissolve in or readily break apart upon immersion in water. A wide variety of materials can be used as the substrate.

Non-limiting examples of suitable substrates include non-woven substrates, woven substrates, hydroentangled substrates, air-entangled substrates and the like.

Preferred embodiments employ non-woven substrates since they are economical and readily available in a variety of materials. By non-woven is meant that the layer is comprised of fibres which are not woven into a fabric but rather are formed into a sheet, particularly a tissue. The fibres can either be random (i.e., randomly aligned) or they can be carded (i.e. combed to be oriented in primarily one direction). Furthermore, the non-woven substrate can be composed of a combination of layers of random and carded fibres.

Non-woven substrates may be comprised of a variety of materials both natural and synthetic. By natural is meant that the materials are derived from plants, animals, insects or by-products. By synthetic is meant that the materials are obtained primarily from various man-made materials or from material that is usually a fibrous web comprising any of the common synthetic or natural textile-length fibres, or mixtures thereof.

Non-limiting examples of natural materials useful in the present invention are silk fibres, keratin fibres and

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cellulosic fibres. Non-limiting examples of keratin fibres include those selected from the group consisting of wool fibres, camel hair fibres, and the like. Non-limiting examples of cellulosic fibres include those selected from the group consisting of wood pulp fibres, cotton fibres, hemp fibres, jute fibres, flax fibres, and mixtures thereof. Wood pulp fibres are preferred.

Non-limiting examples of synthetic materials useful in the present invention include those selected from the group consisting of acetate fibres, acrylic fibres, cellulose ester fibres, modacrylic fibres, polyamide fibres, polyester fibres, polyolefin fibres, polyvinyl alcohol fibres, rayon fibres and mixtures thereof. Examples of some of these synthetic materials include acrylics such as Acrilan<sup>®</sup>, Creslan<sup>®</sup>, and the acrylonitrile-based fibre, Orlon<sup>®</sup>; cellulose ester fibres such as cellulose acetate, Arnel<sup>®</sup>, and Acele<sup>®</sup>; polyamides such as Nylons (e.g., Nylon 6, Nylon 66, Nylon 610 and the like); polyesters such as Fortrel<sup>®</sup>, Kodel<sup>®</sup>, and the polyethylene terephthalate fibres, Dacron<sup>®</sup>; polyolefins such as polypropylene, polyethylene; polyvinyl acetate fibres and mixtures thereof.

Non-woven substrates made from natural materials consist of webs or sheets most commonly formed on a fine wire screen from a liquid suspension of the fibres.

Non-woven substrates made from synthetic materials useful in the present invention can be obtained from a wide variety of

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commercial sources. Non-limiting examples of suitable non-woven layer materials useful herein include HEF 40-047, an apertured hydroentangled material containing about 50% rayon and 50% polyester, and having a basis weight of about 43 grams per square yard (gsy), available from Veratec, Inc., Walpole, MA; HEF 140-102, an apertured hydroentangled material containing about 50% rayon and 50% polyester, and having a basis weight of about 56 gsy, available from Veratec, Inc., Walpole, MA; Novenet® 149-191, a thermo-bonded grid patterned material containing about 69% rayon, about 25% polypropylene, and about 6% cotton, and having a basis weight of about 100 gsy, available from Veratec, Inc., Walpole, MA; HEF Nubtex® 149-801, a nubbed, apertured hydroentangled material, containing about 100% polyester, and having a basis weight of about 70 gsy, available from Veratec, Inc. Walpole, MA; Keybak® 951V, a dry formed apertured material, containing about 75% rayon, about 25% acrylic fibres, and having a basis weight of about 43 gsy, available from Chicopee Corporation, New Brunswick, NJ; Keybak® 1368, an apertured material, containing about 75% rayon, about 5% polyester, and having a basis weight of about 39 gsy, available from Chicopee Corporation, New Brunswick, NJ; Duralace® 1236, an apertured, hydroentangled material, containing about 100% rayon, and having a basis weight from about 40 gsy to about 115 gsy, available from Chicopee Corporation, New Brunswick, NJ; Duralace® 5904, an apertured, hydroentangled material, containing about 100% polyester, and having a basis weight from about 40 gsy to about 115 gsy, available from Chicopee Corporation, New

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Brunswick, NJ; Sontaro<sup>®</sup> 8868, a hydroentangled material, containing about 50% cellulose and about 50% polyester, and having a basis weight of about 60 gsy, available from Dupont Chemical Corp.

5

The substrates used in the present invention need not be formed of fibres. They may be cast as plastic films such as polyethylene, polyester, polyurethane, polyvinyl chloride, polyamide, cellophane, or metallic foils.

10

The water insoluble substrates of the present invention can comprise two or more layers. They may be of similar construction or have different texture and abrasiveness. The differing textures can result from the use of different combinations of materials or from the use of a substrate having a more abrasive side for exfoliation and a softer, absorbent side for gentle cleansing.

15

A further important element of cosmetic strips according to the present invention is the adhesive composition deposited onto the substrate. The adhesive may be of the pressure sensitive variety or may be a dry-to-the-touch film whose taticity is generated by adding a small amount of water at the point of use.

20

25

Pressure sensitive adhesives may be formed from a variety of natural and synthetic adhesive polymers. The natural ones may be based on starch or modified starches. Synthetic adhesives include polyvinyl acetate, polyvinyl chloride, polyurethane, polyamide, but most especially acrylic-based polymers. The acrylics may be homo- or co-polymers (the

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latter indicating at least two different monomer units within the polymer chain). Typical monomers for use in acrylic-based polymers include acrylic acid, methacrylic acid, ethylacrylate, methylacrylate, butylacrylate and combinations thereof. Suitable monomers include those available under the trademark Gelva® series sold by Monsanto and the Duro-Tak® series sold by the National Starch and Chemical Company. Most preferred are acrylic polymers available from Lohmann Therapie Systeme, Germany. Silicone-based polymers may also be employed, such as Bio-Psa silicones sold by the Dow Corning Corporation.

Release or backing liners are usually placed over the adhesive layer. The release liner should have a surface that is easily stripped off or released prior to use of the strip. Suitable materials for this liner include polyvinylchloride, polyester, polyvinylidene chloride, polystyrene, polyethylene and paper, all of which are preferably but not necessarily coated with a silicone formulation.

Another type of adhesive suitable for use in the present invention is a dry-to-the-touch substance. In a dry state, the adhesive composition is non-tacky to the touch. The adhesive is activated by either directly wetting the composition on the sheet or indirectly by wetting the face in areas to be contacted by the composition. In either instance, the wetting agent interacts with the adhesive composition so it becomes tacky and sufficiently mobile to flow into skin pores. Pure water is the preferred wetting agent. However, other fluid systems or gels could be

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employed. Suitable fluids would include alcohols such as ethanol, propanol, propylene glycol, polyethylene glycol, polypropylene glycol and mixtures of these alcohols with water, mixtures of these alcohols with water are preferred.

5 Gels would normally consist of fluid (particularly water) and structuring agents such as carbomer.

Subsequent to wetting, the adhesive composition is allowed to dry over the area of treatment. During drying the  
10 keratotic plugs stickingly adhere to the composition. Advantageously the drying period ranges from 1 minute to 5 hours, preferably from 5 minutes to 1 hour, optimally from 10 to 20 minutes. Thereafter, the dried composition with adhered plugs is peeled from the skin.

15

The adhesive composition will include a polymer which may either be anionic, nonionic, cationic, amphoteric or mixtures thereof. Further, there may be utilised combinations of different polymers from within the same  
20 type. Examples of nonionic polymers suitable for film deposition are the copolymers of vinyl acetate and crotonic acid, terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; copolymers  
25 of methyl vinyl ether and maleic anhydride (molar ratio about 1.1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers, terpolymers, etc., containing acrylic acid or methacrylic acid, esters of  
30 acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms such as methyl



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methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl methacrylate, n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and behenyl acrylate, glycols having from 1 to 5 6 carbon atoms such as hydroxypropyl methacrylate and hydroxyethyl acrylate, styrene, vinyl caprolactam, vinyl acetate, acrylamide, alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group such as methacrylamide, t-butyl acrylamide and n-octyl acrylamide, 10 and other compatible unsaturated monomers. One specific example is the emulsion polymerized terpolymer of methacrylic acid, n-butyl acrylate and ethyl acrylate (e.g., in a weight percent ratio of 31:42:27, respectively).

15 Further examples of nonionic film forming adhesive polymers are homopolymers of N-vinylpyrrolidone and copolymers of N-vinylpyrrolidone with compatible nonionic monomers such as vinyl acetate and terpolymers of ethyl acrylate, butyl methacrylate and methyl methacrylate. Nonionic polymers 20 containing N-vinylpyrrolidone in various weight average molecular weights are available commercially from ISP Corporation such as homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 under the trademark PVP K-90 and those having an average molecular 25 weight of about 1,000,000 sold under the trademark of PVP K-120. Particularly preferred is poly(methyl vinyl ether/maleic anhydride) as an unneutralized resin available from ISP Corporation under the trademark Gantrez® S-97 BF and polyvinylformamide available from the National Starch 30 and Chemical Company, a division of ICI.

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Anionic film forming adhesive polymers are often derived from the nonionic types which include carboxylic acid functions. Alkaline agents are employed to neutralize the carboxylic acid or anhydride transforming them into anionic salts. Examples of suitable neutralizing agents include

5 2-amino-2-methyl-1,3-propanediol (AMPD);  
2-amino-2-ethyl-1,3-propanediol (AEPD);  
2-amino-2-methyl-1-propanol (AMP); 2-amino-1-butanol (AB);  
monoethanolamine (MEA); diethanolamine (DEA);  
10 triethanolamine (TEA); monoisopropanolamine (MIPA);  
diisopropanol-amine (DIPA); triisopropanolamine (TIPA); and  
dimethyl stearamine (DMS). Most preferred is AMP.

Particularly preferred anionic polymers are the salts of

15 poly(methyl vinyl ether/maleic anhydride) and polystyrene sulfonic acid. The former is obtained by at least partial neutralization of Gantrez® S-97 BF and the latter available from the National Starch & Chemical Company under the trademarks Versa TL-501 and Flexan® 130 having respective

20 molecular weights of about 500,000 and 100,000. Other polymer films that may be employed and are commercially available are listed in the Table below.

**TABLE**

<b>POLYMER TRADEMARKS (SUPPLIER)</b>	<b>CTFA DESIGNATIONS</b>
Resyn® 28-1310 (NSC)	Vinyl acetate/crotonic acid copolymer
Resyn® 28-2930 (NSC)	Vinyl acetate/crotonic acid/vinyl neodecanoate copolymer
Resyn® 28-2913 (NSC)	Vinyl acetate/crotonic acid/vinyl neodecanoate copolymer
Versatyl® 40 (NSC)	Octylacrylamide/acrylates copolymer
Versatyl® 42 (NSC)	Octylacrylamide/acrylates copolymer
Experimental Resin (NSC)	Vinyl acetate/vinyl neodecanoate/maleic half-ester
Ultrahold-8® (BASF)	Acrylate/acrylamide copolymer
Luviset® CAP (BASF)	Vinyl acetate/crotonic acid/vinyl propionate copolymer
PVP K-30 (ISP)	PVP
PVP/VA E-335 (ISP)	PVP/Vinyl acetate copolymer
PVP/VA E-735 (ISP)	PVP/Vinyl acetate copolymer
Gantrez® ES-225 (ISP)	Ethyl ester of PVM/MA copolymer
Gantrez® ES-425 (ISP)	Butyl ester of PVM/MA copolymer
Gaffix® VC-713 (ISP)	Vinyl caprolactam/PVP/dimethyl aminoethyl methacrylate copolymer

Cationic adhesive polymers suitable for the present  
5 invention may be prepared as homo- or copolymers from  
monomers including:

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Dimethyl aminoethyl acrylate (DMAEA), dimethylaminoethyl methacrylate (DMAEMA), dimethylaminopropylacrylamide (DMAPAAm), and dimethylaminopropyl methacrylamide (DMAPMAAm) 5 which are all (meth)acrylamides or (meth)acrylic acid esters having a dialkylamino group;

Dimethylaminostyrene (DMASt) and dimethylaminomethylstyrene (DMAMSt) and the like which are styrenes having a 10 dialkylamino group;

4-vinyl pyridine and 2-vinyl pyridine which are vinyl pyridines; and

15 Quaternized products of these with a known quaternizing agent such as alkyl halide, benzyl halide, alkyl or aryl sulfonic acid, or dialkyl sulfate.

Among suitable amphoteric adhesive polymers are those 20 derived from monomers such as:

N-(3-sulfopropyl)-N-acryloyloxyethyl-N,N-dimethylammonium betaine, N-(3-sulfopropyl)-N-methacroylamidepropyl-N,N-dimethylammonium betaine, N-(3-carboxymethyl)-N- 25 methacroylamidepropyl-N,N-dimethylammonium betaine and N-carboxymethyl-N-methacroyloxyethyl-N,N-dimethylammonium betaine.

When the salt forming group of the cationic and amphoteric 30 polymers is not ionized, it is preferred to ionize it via neutralization with known acids such as hydrochloric acid

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and sulphuric acid which are inorganic acids; acetic acid, propionic acid, lactic acid, succinic acid, glycol acid which are organic acids, or with known bases such as triethylamine, trimethylamine which are tertiary amines; ammonia; or sodium hydroxide.

The relative amount of water-insoluble substrate to adhesive composition may vary, as a weight ratio, from about 1,000:1 to about 1:1,000, preferably from about 100:1 to about 1:100, optimally from 20:1 to about 1:20, more optimally from about 5:1 to about 1:5 by weight.

The thermochromic substance may be present in the cosmetic strip in an amount from about 0.0001 to about 30%, preferably from about 0.001 to about 20%, optimally from about 0.01 to about 5% by the total weight of the cosmetic strip.

Advantageously, the adhesive composition may include an agent reactive with water (or perspiration) to generate a change of temperature. The agent should be capable of an exothermic or endothermic temperature jump preferably from about 2° to about 30°C, more preferably from about 5° to about 20°C, even more preferably from about 10° to about 15° C.

Illustrative of the exothermic reaction inducing agents are anhydrous silica, alumina, aluminosilicates and combinations thereof. Particularly preferred are zeolites such as Zeolite A available from PQ Corporation and Cab-O-Sil® fumed

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silica available from the Cabot Corporation. Examples of endothermic agents are ammonium chloride and xylitol. The amount of these substances within the adhesive composition may range from about 0.1 to about 70%, optimally from about 1 to about 40% by weight. When incorporating a water sensitive temperature change inducing agent, care should be taken to maintain the strip within packaging (e.g. sealed pouch or packet) that avoids exposure to moisture or at least excessive moisture before use.

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A variety of skin treatment agents may be formulated with the adhesive compositions. These agents may include moisturizers, preservatives, herbal extracts, vitamins, anti-irritant agents, emulsifiers and anti-keratolytic agents.

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Polyhydric alcohols, also known as polyols, and water are the most useful moisturizers. Representative polyols include glycerine, diglycerine, propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol and derivatives thereof, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,2-butylene glycol, 1,2,6-hexanetriol, isoprene glycol, 2-methyl-1,3-propanediol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof. The amount of the polyol and/or water may range from about 0.1 to about 95%, preferably from about 1 to about 50%, more preferably from about 1.5 to about 20%, optimally from about 3 to about 10% by weight of the adhesive composition.

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Preservatives can desirably be incorporated into the adhesive compositions to protect against the growth of potentially harmful microorganisms. Suitable preservatives include alkyl esters of para-hydroxybenzoic acid, hydantoin derivatives, propionate salts, and a variety of quaternary ammonium compounds. Cosmetic chemists are familiar with appropriate preservatives and routinely choose them to satisfy the preservative challenge test and to provide product stability. Particularly preferred preservatives are phenoxyethanol, methyl paraben, propyl paraben, imidazolidinyl urea, sodium dehydroacetate and benzyl alcohol. Preservatives are preferably employed in amounts ranging from 0.01% to 2% by weight of the composition.

Herbal extracts which may be used in the present invention include Roman Chamomile, Green Tea, Scullcap, Nettle Root, Swertia Japonica, Fennel, Anise, Arnica, Calandula, Coltsfoot, Cornflower, Elder, Gentian, Hawthorn, Lavender, Linden, Myrrh, Oat, Rose, Sweet Clover, Sandalwood, Vetiver, Tulsi, Kamala, Eucalyptus, St. John's Wort and Aloe Vera extracts. The amount of each extract used may range from about 0.00001 to about 1%, preferably from about 0.01 to about 0.5%, optimally from about 0.05 to about 0.2% by weight of the adhesive composition.

Vitamins useful in products of the present invention include vitamin E acetate, vitamin C, vitamin A palmitate, panthenol and any of the vitamin B complexes. Anti-irritant agents may also be present including those of alpha-bisabolol and potassium glycyhrrizinate, each vitamin or anti-irritant agent being present in amounts ranging from about 0.001 to

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about 0.5%, preferably from about 0.01 to about 0.1% by weight of the adhesive composition.

Emulsifiers may also be incorporated into the cosmetic strips of this invention. These emulsifiers may be anionic, nonionic, cationic, amphoteric or a combination thereof. Useful nonionic type emulsifiers include C<sub>10</sub>-C<sub>20</sub> fatty alcohols or acid hydrophobes condensed with from 2 to 100 moles of ethylene oxide or propylene oxide per mole of hydrophobe; C<sub>2</sub>-C<sub>10</sub> alkyl phenols condensed with from 2 to 20 moles of alkylene oxide; mono- and di-fatty acid esters of ethylene glycol; fatty acid monoglyceride; sorbitan, mono- and di-C<sub>8</sub>-C<sub>20</sub> fatty acids; block copolymers (ethylene oxide/propylene oxide); and polyoxyethylene sorbitan as well as combinations thereof. Alkyl polyglycosides and saccharide fatty amides (e.g. methyl gluconamides) are also suitable nonionic emulsifiers. Amounts of the emulsifiers may range from about 0.1 to about 30%, preferably from about 0.5 to about 10% by weight of the adhesive composition.

Anti-keratolytic agents may also be incorporated into the adhesive compositions. Typical of these agents are the alpha and beta hydroxycarboxylic acids. The alpha-hydroxycarboxylic acids include glycolic acid, malic acid, lactic acid and mixtures thereof as well as their salts such as alkali metal and ammonium salts thereof. The most preferred beta hydroxycarboxylic acid is salicylic acid. Amounts of these anti-keratolytic agents may range from about 0.01 to about 15%, preferably from about 1 to about 12% by weight of the adhesive composition.



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Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material ought to be understood as modified by the word "about".

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise illustrated.

#### **EXAMPLE 1**

A dry-to-the-touch strip was prepared for use in removing keratotic plugs from skin pores. The strip employed was a 70:30 rayon/polyester non-woven fabric available from Dupont. Poly(methyl vinyl ether maleic anhydride), commercially available as Gantrez S-97® was employed as the adhesive. The resin was dispersed in water along with Chromicolor AQ Ink (Type 27), titanium dioxide, silica and 2-amino-2-methyl-1-propanol (AMP). The mixture was coated by a knife-over-roll onto the non-woven substrate. After coating, the strip and adhesive composition was dried at 75°C in a convection oven. The dried sheet was then cut into small strips. The adhesive composition was dry-to-the-touch and had a composition as listed in Table I.

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TABLE I

COMPONENT	WEIGHT %
Gantrez S-97®	88
AMP	7
Chromicolor AQ Ink (Type 27)	3.9
Titanium Dioxide	1
Silica	0.1

5 EXAMPLE 2

Another dry-to-the-touch strip for removing keratotic plugs from skin pores was prepared employing a polyester/cellulose wet layered non-woven fabric. Poly(vinylformamide) available from the National Starch and Chemical Company was used as the adhesive in combination with Chromicolor AQ Ink (Type 27), titanium dioxide, silica, water, vitamin C (ascorbic acid), glycerin, dimethicone copolyol, methoxypropyl glucamide and disodium EDTA. The mixture was coated by a knife-over-roll onto the non-woven substrate. After coating, the strip and adhesive composition were dried at 75°C in a convection oven. The dried sheet was then cut into small strips. The adhesive composition was dry-to-the-touch and had a composition as listed in Table II.

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**TABLE II**

COMPONENT	WEIGHT %
Polyvinylformamide	88
Chromicolor AQ Ink (Type 27)	2.2
Titanium Dioxide	1
Disodium EDTA	0.8
Methoxypropylgluconamide	0.7
Silica	2.0
Water	1.5
Glycerin	1.5
Dimethicone Copolyol	1.3
Vitamin C	1.0

**5    EXAMPLE 3**

This example illustrates a cationic type dry-to-the-touch strip used for the removal of keratotic plugs from skin pores. The substrate employed was a 100% cellulose non-woven fabric. Components of the adhesive as listed in Table III were combined in isopropanol with stirring and after full dispersion of the components coated onto the cellulose substrate. Thereafter the system was dried to remove the isopropanol solvent. The dried sheet was then cut into small strips.

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**TABLE III**

COMPONENT	WEIGHT %
Poly-2-acrylamide-2-methylpropane sulphonate	32.0
Zeolite	45.0
Glycerin	15.0
Perfume	5.0
Polyoxyethylene Hydrogenated Castor Oil (60 EO Adduct)	2.0
Chromicolor AQ Ink	1.0

**5    EXAMPLE 4**

This Example illustrates an embodiment utilizing a pressure sensitive adhesive type of dermal patch. A polypropylene film was employed as the substrate. A silicone pressure sensitive adhesive was deposited onto the film. The silicone pressure sensitive material has previously been prepared by condensing a siloxane resin copolymer with hydroxyl terminated polydimethyl siloxane in xylene solution, in the presence of anhydrous ammonium, at about 115°C. The resultant silicone adhesive in an amount of 85% was combined with 5% ascorbic acid and 10% Chromicolor AQ Ink (Type 27). A Mylar® backing sheet was placed over the pressure-sensitive adhesive composition for storage and shipping purposes.

**20    EXAMPLE 5**

Another pressure sensitive adhesive strip for topical treatment of acne was prepared. A breathable polyurethane

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film (Bertek Medfilm 390) served as a substrate sheet for an adhesive composition. An easy release silicon coated polystyrene film was then placed over the adhesive layer. The final thickness of the dried matrix was between 75 and 150  $\mu\text{m}$ . Circular patches were then cut from the resultant multi-layered laminate. The formulation of the adhesive composition was as outlined in Table IV.

**TABLE IV**

COMPONENT	WEIGHT %
Polyacrylic Adhesive Resin	96
Salicylic Acid	0.6
Glycolic Acid	0.4
Sorbitan Monooleate	1.0
Chromicolor AQ Ink (Type 26)	1.0
Alpha-bisabolol	0.5
Potassium Glycyrrhizinate	0.5

**EXAMPLE 6**

Microencapsulated pellets of Chromicolor AQ Ink (5%) were combined with polypropylene pellets and extruded through a plastic extruder to form a sheet of thermocolor impregnated plastic substrate. Onto this substrate was deposited an acrylic based pressure-sensitive adhesive formulated with 2% lactic acid. Over the adhesive layer was applied a release liner covering the tacky adhesive until ready for use when the liner is peeled away.

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**EXAMPLE 7**

An aqueous dispersion of Chromicolor AQ was spread onto a cellulose non-woven substrate sheet. The sheet was dried in  
5 a convection oven to remove water and the thermochromic agent deposited into the cellulose substrate. Thereafter pressure-sensitive acrylic-based resin was applied. Mixed within the acrylic-based resin was 40% of powdered, finely dispersed zeolite and 2% salicylic acid. A release liner  
10 film was applied over the adhesive. When ready for use, the liner was removed, and the adhesive strip applied to the face. Over several hours, perspiration penetrates the adhesive layer, interacts with the zeolite and thereby emits a heat of reaction. This reaction causes the thermochromic  
15 agent impregnated into the cellulosic strip to turn from blue to colorless. The color change indicates to a user the minimum time required for the strip to release its active amount of anti-acne salicylic acid agent.

20 The foregoing description and Examples illustrate selected embodiments of the present invention. In the light thereof variations and modifications will be suggested to one skilled in the art, all of which are within the spirit and purview of this invention.

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**CLAIMS:**

1. An adhesive cosmetic strip comprising:
  - (i) a flexible water-insoluble substrate;
  - 5 (ii) an adhesive composition deposited onto the substrate; and
  - (iii) a non-liquid crystal thermochromic substance incorporated into at least one of the substrate and the adhesive composition,
- 10 the thermochromic substance changing colour in response to a change of temperature after the strip has contacted a user's skin.
- 15 2. A strip according to claim 1, wherein the adhesive is selected from dry-to-the-touch and pressure-sensitive tacky adhesives.
- 20 3. A strip according to claim 1 or 2, wherein the thermochromic substance is a combination of an acid-responsive chromogenic material and an acidic material.
- 25 4. A strip according to any one of the preceding claims, wherein the thermochromic substance is incorporated into the substrate.
5. A strip according to any one of the preceding claims, wherein the thermochromic substance is incorporated into the adhesive composition.

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6. A strip according to claim 3, wherein the acid-responsive chromogenic material is selected from the group consisting of triphenylmethanephthalide compounds, phthalide compounds, phthalan compounds, acyl-leucomethylene blue compounds, fluoran compounds, triphenylmethane compounds, diphenylmethane compounds and spiropyran compounds.
7. A strip according to claim 3, wherein the acidic material includes a benzotriazole compound or a phenol compound.
8. A strip according to any one of the preceding claims, wherein the adhesive composition further comprises a skin treatment agent.
9. A strip according to claim 8, wherein the skin treatment agent is selected from the group consisting of herbal extracts, Vitamins and keratolytic agents.
10. A strip according to claim 9, wherein the keratolytic agent is salicylic acid.
11. A strip according to any of the preceding claims, wherein the acid-responsive chromogenic material is present at a level of 0.1 to 50% by weight of the thermochromic substance.
12. A strip according to any of the preceding claims, wherein the acidic material is present at a level of 0.1 to 50% by weight of the thermochromic substance.



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13. A strip according to any of the preceding claims,  
wherein the thermochromic substance is microencapsulated.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/06799

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 18098 A (THERMOTONE NAILS LTD) 16 September 1993 (1993-09-16) abstract page 4, line 16 - line 22 ---	1-13
A	WO 97 48387 A (LAVIPHARM SA (GR)) 24 December 1997 (1997-12-24) claims ---	1,2,8-10
A	US 4 719 198 A (SATO MASUHIKO ET AL) 12 January 1988 (1988-01-12) claims --- -/--	1-7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

12 December 2000

Date of mailing of the international search report

21/12/2000

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06799

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 199902 Derwent Publications Ltd., London, GB; Class A82, AN 1999-012584 XP002155133 &amp; JP 10 265772 A (NICHIBAN KK), 6 October 1998 (1998-10-06) abstract</p> <p>-----</p>	1-7

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06799

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9318098	A	16-09-1993	AU 3807493 A	05-10-1993
WO 9748387	A	24-12-1997	GR 1002807 B	13-11-1997
			US 5976565 A	02-11-1999
			AU 3340997 A	07-01-1998
			BR 9709920 A	11-01-2000
			CA 2258242 A	24-12-1997
			CN 1226160 A	18-08-1999
			EP 0917461 A	26-05-1999
			FR 2750050 A	26-12-1997
			JP 2000513347 T	10-10-2000
			NO 985938 A	18-02-1999
			PL 330848 A	07-06-1999
US 4719198	A	12-01-1988	JP 57201691 A	10-12-1982
			DE 3265598 D	26-09-1985
			EP 0066813 A	15-12-1982
JP 10265772	A	06-10-1998	NONE	